Crystal Transformation and Development of Tensile Properties upon Drawing of Poly(L-lactic acid) by Solid-State Coextrusion: Effects of Molecular Weight

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Summary: Melt-crystallized films of poly(L-lactic acid) (PLLA) with M_v in the range of $3.8 \sim 46 \times 10^4$ consisting of α-form crystals were uniaxially drawn by solid-state coextrusion. The effects of M_v, extrusion draw ratio (EDR), and extrusion temperature (T_{ext}) on the crystal/crystal transformation from α- to β-form crystals and the resultant tensile properties of drawn products were studied. The crystal transformation proceeded with EDR and more rapidly for the higher M_v's. Furthermore, the crystal transformation proceeded most rapidly with EDR at a T_{ext} around 130 °C, independently of the M_v's. As a result of the optimum combination of processing variables influencing the the crystal transformation (M_v, T_{ext}, and drawability), highly oriented films consisting of β-form crystals alone were obtained by coextrusion of higher M_v samples at T_{ext}'s slightly below the melting temperature ($150 \sim 170$ °C) and at higher EDR's > 11. Both the tensile modulus and strength increased rapidly with EDR. The modulus at a given EDR was slightly higher for the samples with higher M_v's. In contrast, the strength at a given EDR was remarkably higher for the higher M_v's. The highest tensile modulus of 8.0 GPa and strength of 500 MPa were obtained with the sample of the highest M_v of 46×10^4 coextruded at 170 °C to the highest EDR of 14.

Keywords: coextrusion; crystal transformation; infrared spectroscopy; poly(L-lactic acid); tensile modulus and strength

Introduction

Poly(L-lactic acid) (PLLA) attracts considerable interest from both fundamental and industrial viewpoints because it can be synthesized from renewable resources, such as corn and potato.[1–3] Since PLLA is biodegradable and biocompatible, this polymer has been used for biomedical applications.[4–6] Since PLLA has good mechanical properties with a high melting temperature (~175 °C), its application for more general purposes as an environmentally and economically feasible polymer has been evaluated.[7–9]

PLLA takes three crystal forms[10–16] depending on the crystallization and drawing conditions. The most common polymorph, the α form (pseudo-orthorhombic,[10] pseudo-hexagonal,[11,12] or orthorhombic[13–15]) has a 10_7 helical chain conformation and is obtained by crystallization from melt or solutions. The β form[12,16] (orthorhombic[12] or trigonal[16]) is known to take a 3_2 helical conformation and is obtained by drawing of a PLLA film consisting of α-form crystals. Recently, it was found that a new γ-form grows on a hexamethylbenzene

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crystal by epitaxial crystallization.[17] This polymorph also has an orthorhombic unit cell containing two regularly packed antiparallel 3_2 helices.

Eling et al.[10] reported that β crystals were generated upon tensile drawing at a high temperature to a higher draw ratio (DR), whereas the drawing at a low temperature and/or a low DR produced α crystals. Thus, the drawn products of PLLA commonly consist of α crystals or a mixture of α and β crystals. In our previous studies,[18–20] the effects of draw ratio (DR), draw temperature, draw stress, and draw techniques on the crystal/crystal transformation from α- to β-form crystals were discussed. It was found that α crystals steadily transformed into β-form crystals with increasing DR. The crystal transformation proceeded most efficiently for drawing at 130–140 °C by both tensile drawing and solid-state extrusion. It was also found that the efficiency of the transformation, as evaluated from the amount of β-form crystals formed at a given DR, was higher at a higher draw stress or a higher extrusion pressure at a given draw temperature.[19,20]

The physical and mechanical properties of a given polymer, in general, strongly depend on the morphology, crystal structure, and sample molecular weight. In this article, thus, we discuss the effects of molecular weight on the crystal/crystal transformation and the development of tensile properties upon drawing of PLLA samples by solid-state coextrusion in the wide ranges of extrusion temperatures.

Experimental Section

Samples

Four PLLA samples with viscosity-average molecular weights, M_v's, in the ranging of $3.8 \sim 46 \times 10^4$ were prepared by ring- opening polymerization of L-lactide.[21] Commonly the molecular weight of a PLLA sample significantly decreases upon compression molding from the melt, especially at higher temperatures. Therefore, the effect of molding conditions on the molecular weight degradation was examined first for a PLLA sample with $M_v = 46 \times 10^4$ to determine the optimum conditions which minimize the molecular weight degradation upon the molding. Based on the results shown in Table 1, the sample pellets were dried at 100 °C for 24 h before molding, added with 0.5 wt% of an antioxidant, *dl*-α-tocophenol (vitamin E), and compression molded into films at 190 °C, the lowest temperature at which uniform films could be obtained, under a N_2 atmosphere. The M_v's of the initial samples and the films molded under the optimum conditions are shown in Table 2 for a series of the samples used in this work. The crystallinities and T_m's of the films are also included in Table 2.

The intrinsic viscosity of a PLLA sample was measured in chloroform at 25 °C and

Table 1.
Viscosity-average molecular weights (M_v's) of the films prepared by compression-molding of H-M_v pellets at 190 °C under various conditions.

	Pellets	Film1	Film2	Film3	Film4	Film5
Antioxidant[a]	—	×	○	○	○	○
Atmosphere	—	Air	Air	N_2	N_2	N_2
M_v ($\times 10^{-4}$)	46	22	30	31	35	35
Drying time (h)[b]		24	24	8	24	48

[a] *dl*-α-Tocopherol (vitamin E).
[b] Pellets were dried in vacuo at 100 °C for different time.
○: 0.5 wt% of an antioxidant was added before the melt-molding at 190 °C.
×: No antioxidant was added.

Table 2.
Molecular weights (M_v) of the initial PLLA pellets and melt-molded films.

	L-M_v1	L-M_v2	M-M_v	H-M_v
Pellets, M_v ($\times 10^{-4}$)	3.8	5.0	9.6	46
Films[a], M_v ($\times 10^{-4}$)	3.2	4.2	8.9	35
Crystalinity (wt %)	56	55	54	49
T_m (°C)[a]	168.7	170.2	177.5	181.3

The films were prepared by compression-molding of the pellets under the optimum conditions; dried *in vacuo* at 100 °C for 24 h, added with 0.5 wt% of an antioxidant, and then compression-molded at 190 °C under a N_2 atmosphere.

[a] : DSC melting peak temperatures determined at a heating rate of 10 °C/min.

an M_v was calculated according to the following equation.[22]

$$[\eta] = 5.45 \times 10^{-4} \times M_v^{0.73} \quad (1)$$

Drawing

Draw was made by solid-state coextrusion. For this, a strip of PLLA with 10 mm width and 70 mm length was placed between two split billet halves of an appropriate polymer that was selected from 7 polymers depending on the required T_{ext} and extrusion pressure (P_{ext}), and the assembly was coextruded through a conical brass die. These polymers include two kinds of linear low-density polyethylenes having different MFR's of 50 and 8, high-density polyethylene, poly(4-methyle-1-pentene) (P4M1P), copolymer of P4M1P, poly(chlorotrifluoroethylene), and polytetrafluoroethylene. The extrusion rate was ~1 cm/min independently of the extrusion conditions such as an EDR and T_{ext}.

Characterization

The crystal transformation from α– to β–form crystals was followed by infrared (IR) spectroscopy. Polarized spectra were recorded using a JEOL Fourier transform infrared spectrometer (JRS-FT7000W) at a resolution of 1 cm^{-1} and room temperature. An oriented film consisting of α-form crystals (10_7 helix) or β-form crystals (3_2 helix) exhibited absorption bands at 923 cm^{-1} (α-form) or 912 cm^{-1} (β-form), respectively, that were assigned to the CH_3 rocking mode having the transition moment perpendicular to the chain axis.[19,21] The total absorbance A_0 for an oriented sample was corrected for the chain orientation.[19,23]

The tensile modulus and strength on the fiber axis were measured at strain rates of 1×10^{-3} s^{-1} and 1×10^{-2} s^{-1}, respectively, at room temperature. Measurements were made at least five times for a given sample. The modulus was determined from the initial slope of the stress/strain curve at a low strain (<0.1%). The cross-sectional area of a sample was calculated from the sample weight, length, and measured density. The weight-percent crystallinity (X_c) was calculated from the sample density.[18]

Results and Discussion

Drawing by Solid-State Coextrusion

Figure 1 shows the maximum achieved EDR (EDR_{max}) as a function of T_{ext} for the melt-crystallized films of four PLLA samples having different M_v's. Commonly, the EDR_{max} increased with T_{ext}, reaching a maximum at a specific T_{ext} depending on the M_v. At yet higher T_{ext}'s, it suddenly decreased due to the partial melting of the coextrudate after it came out of an extrusion die. Such a variation of the EDR_{max} with the T_{ext} became more prominent with increasing M_v. The T_{ext}, at which the highest EDR_{max} was achieved for a given sample, shifted higher with increasing M_v, and approached a constant temperature of 170°C, near the T_m, for M_v's $\geq 8.9 \times 10^4$. The EDR_{max}'s were 14 for H-M_v and M-M_v

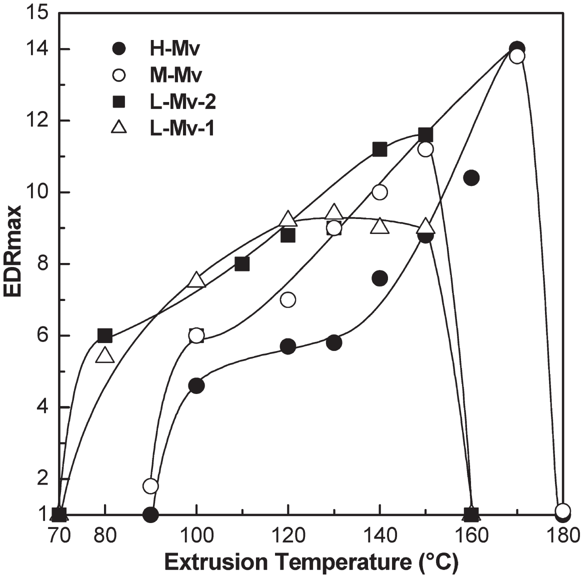

Figure 1.
Maximum achieved EDR (EDR_{max}) as a function of the T_{ext} for L-M_v-1 (△), L-M_v-2 (■), M-M_v (○) and H-M_v (●).

at a $T_{ext} = 170\,^{\circ}C$, 11 for L-M_v-2 at a $T_{ext} = 150\,^{\circ}C$, and 9 for L-M_v-1 at T_{ext}'s $= 120$–$150\,^{\circ}C$, always below their static melting temperatures, T_ms, (see Table 2).

To examine the reason for the low duictility of PLLA, EDR ≤ 14 in this work, the dynamic Young's modulus (E') and loss modulus (E'') were measured as a function of temperature for an unoriented film consisting of α-form crystals ($X_c = 46$ %), a highly oriented and highly crystalline tape consisting of α-form crystals ($X_c = 74$ %), and a highly oriented tape consisting of β-form crystals ($X_c = 50$ %), as shown in Figure 2. These samples from the H-M_v were prepared by slow cooling from the melt, tensile drawing of an amorphous film to a draw ratio of 6 followed by annealing at 170 °C for 1 h, and by solid-state coextrusion of the oriented film at 170 °C and an EDR of 14, respectively. As seen in Figure 2, the dynamic loss modulus E'' for each of the three samples, consisting of α or β crystals, clearly exhibited an α-relaxation at 55–80 °C that was associated with the glass transition and no α_c-relaxation was observed below the T_m showing that neither α nor β crystals exhibit an α_c-relaxation. Therefore, the absence of an α_c-relaxation (or crystal transition) in both α and β crystals is likely the reason for the low ductility of PLLA. [24–26]

Crystal Transformation

The chain orientation of the β-form was significantly higher than that of the α-form crystals within a drawn sample. In this work, thus, the formation of β-form crystals was evaluated from the FT-IR spectroscopy[19,20] which allowed to determine the relative amounts of β-form crystals within a sample even when the degrees of chain orientation of the α- and the β-form crystals were different within the sample.

Figure 3 shows FT-IR spectra for an EDR series prepared by solid-state coextrusion of the H-M_v at a T_{ext} of 170 °C. As the profile for each of the IR bands at 912 and 923 cm^{-1} was well approximated by a Gaussian function, the observed IR spectra were resolved into the appropriate peaks at 912 and 923 cm^{-1} assuming Gaussian functions that were determined from the samples consisting of only α- or β-form

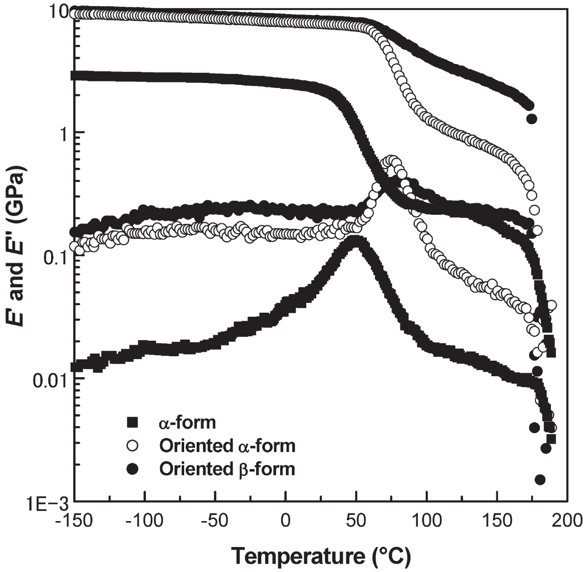

Figure 2.
Dynamic Young's modulus (E′) and loss modulus (E″) as a function of temperature measured at 11 Hz. ■, a randomly oriented α-form film ($X_c = 46\%$); ○, a highly oriented and highly crystalline α-form film ($X_c = 74$ %); and ●, a highly oriented β-form film ($X_c = 50$ %).

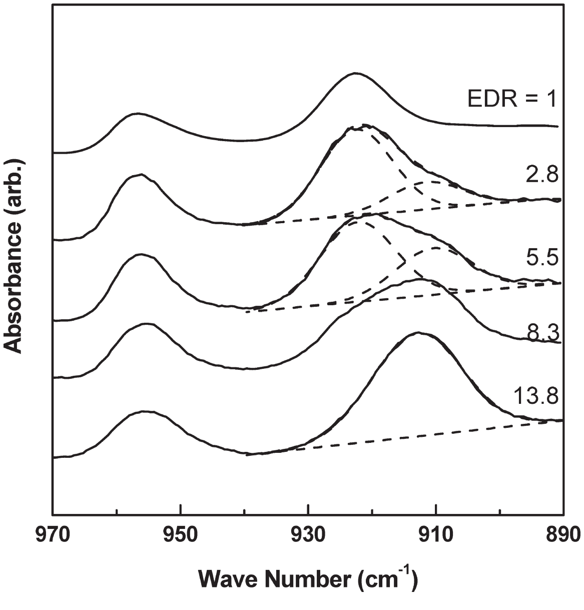

Figure 3.
Infrared spectra in the 890–970 cm^{-1} region for an EDR series of H-M_v prepared at a $T_{ext} = 170$ °C. The spectra were corrected for the chain orientation. The observed (solid line) and the decomposed spectra assuming Gaussian functions for the 912 cm^{-1} band ascribed to β-form crystals and the 923 cm^{-1} band ascribed to α-form crystals (broken lines).

crystals. An absorption band at 923 cm^{-1} characteristic of α-form crystals was observed for an original melt-crystallized film. A new absorption band at 912 cm^{-1} characteristic of β-form crystals appeared at an EDR of 2.8. The intensity of this new band became gradually stronger with increasing EDR and the 912 cm^{-1} band alone was observed at an EDR_{max} of 13.8 indicating that all the α-form crystals had transformed into the oriented β-form crystals.

To evaluate the effect of sample molecular weight on the crystal transformation, the relative amounts of β-form crystals were calculated from the IR spectra[20] as a function of EDR for the specimens prepared by coextrusion of the four M_v's at a T_{ext} of 140 °C. As shown in Figure 4, the fraction of β-form crystals increased linearly with the EDR for all the M_v's and the crystal transformation proceeded more rapidly with increasing sample M_v's. However, the EDR_{max} at a $T_{ext} = 140\,°C$ decreased with increasing the sample M_v. Therefore, the maximum fractions of β-form crystals formed were ~0.93 independently of the M_v's, except for L-M_v-1 sample of the lowest M_v. Such an effect of M_v's on the efficiency of the crystal transformation was also observed at other T_{ext}'s as will be shown below.

Effects of T_{ext} and M_v on the Crystal Transformation

To determine the effects of T_{ext} and M_v on the crystal transformation, the M_v series were coextruded to a constant EDR of 6 in the T_{ext} range of 80–170 °C. The P_{ext} was kept constant at 40 ± 3 MPa for each T_{ext} in the T_{ext} range studied by using split billets of appropriate polymers. Figure 5 shows the fraction of β-form crystals as a function of the T_{ext} for an M_v series coextruded at a constant EDR of 6 and evaluated by the IR intensity ratios of $A_0(912)_\beta/[A_0(912)_\beta + 1.1A_0(923)_\alpha]$. For each M_v, the fraction of β-form crystals at a constant EDR of 6 increased with the T_{ext}, reaching a maximum at around $T_{ext} = 130\,°C$, and at yet higher T_{ext}'s it decreased again. A remarkable effect of M_v on the crystal transformation was observed; i.e., the fractions of

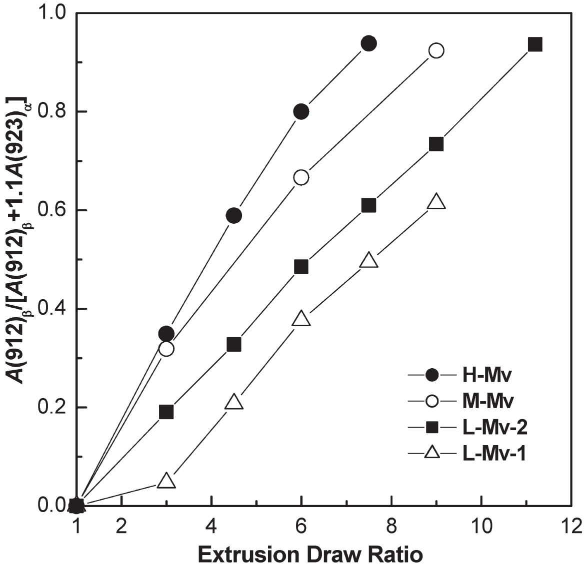

Figure 4.
Relative amounts of β-form crystals as a function of the EDR as evaluated from the IR intensity ratios of $A(912)_\beta/[A(912)_\beta + 1.1A(923)_\alpha]$ for various M_v's. The drawn products were made at a $T_{ext} = 140\,°C$. The symbols are the same as in Figure 1.

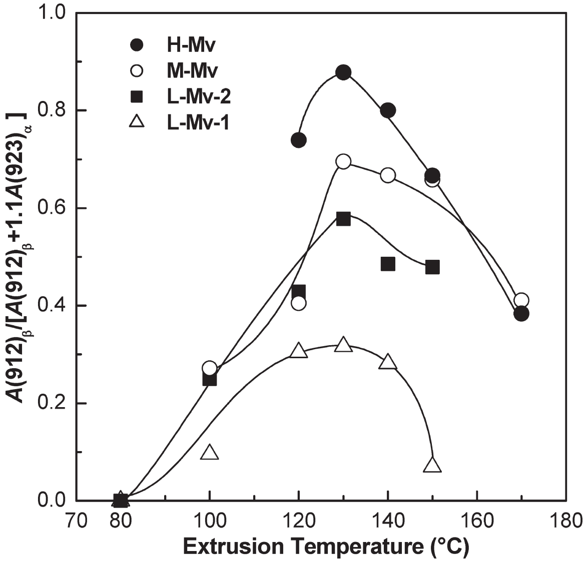

Figure 5.

Effects of T_{ext} and M_v on the formation of β-form crystals as evaluated from the IR intensity ratio of $A(912)_\beta/[A(912)_\beta + A(923)_\alpha]$ for a series of coextrusion drawn products with a constant EDR of 6.

β-form crystals at a given T_{ext} were significantly higher for the higher M_v's.

Figures 6 a and b, respectively, show the relative amounts of β-form crystals as a function of the EDR for the lowest M_v sample of L-M_v-2 and the highest M_v of H-M_v coextruded at different T_{ext}'s in the range of 100–170 °C. Commonly, the relative amounts of the β-form rapidly increased with EDR at all the T_{ext}'s for each of the M_v's. The efficiency of crystal transformation was the highest for the coextrusion at around T_{ext} of 130 °C throughout the EDR ranges and for all the M_v's. It is interesting to note that for a given M_v, the maximum achieved β-form fraction increased with increasing T_{ext}, as a result of the combined effects of the T_{ext} on the ductility increase and the efficiency of the crystal transformation. The samples consisting of β-form crystals alone were obtained by the coextrusion of the H-M_v and M-M_v to EDR's of > 11 at T_{ext}'s ≥ 150 °C.

Mechanical Properties

Figure 7 a and b show the tensile modulus and strength at 25 °C as a function of the EDR for solid-state coextrusion of the films from the four PLLA samples with different M_v's. The coextrusion was made at an optimum T_{ext} at which each sample exhibited the highest ductility. Such an optimum T_{ext} increased with the sample M_v's; T_{ext} of 170 °C for the H-M_v and M-M_v, 150 °C for the L-M_v-2, and 120 °C for the L-M_v-1. The tensile modulus along the fiber axis of the extrudates from a given M_v increased rapidly with the EDR in the lower EDR region (EDR < 5), and more slowly at yet higher EDR's. Although both the H-M_v and the M-M_v were coextruded at the same T_{ext} of 170 °C, the modulus at a given EDR was slightly higher for the higher M_v sample, reflecting the higher draw efficiency associated with the slower relaxation of the coextrusion-induced segmental orientation during the coextrusion drawing. The maximum achieved tensile modulus increased with M_v; i.e., 6.5 GPa for the L-M_v-1, 7.0 GPa for the L-M_v-2, 7.5 GPa for the M-M_v, and 8.0 GPa for the highest M_v sample of H-M_v.

For a given M_v, the tensile strength increased linearly with EDR, reaching a maximum value of 120–500 MPa at the highest achieved EDR, depending on the

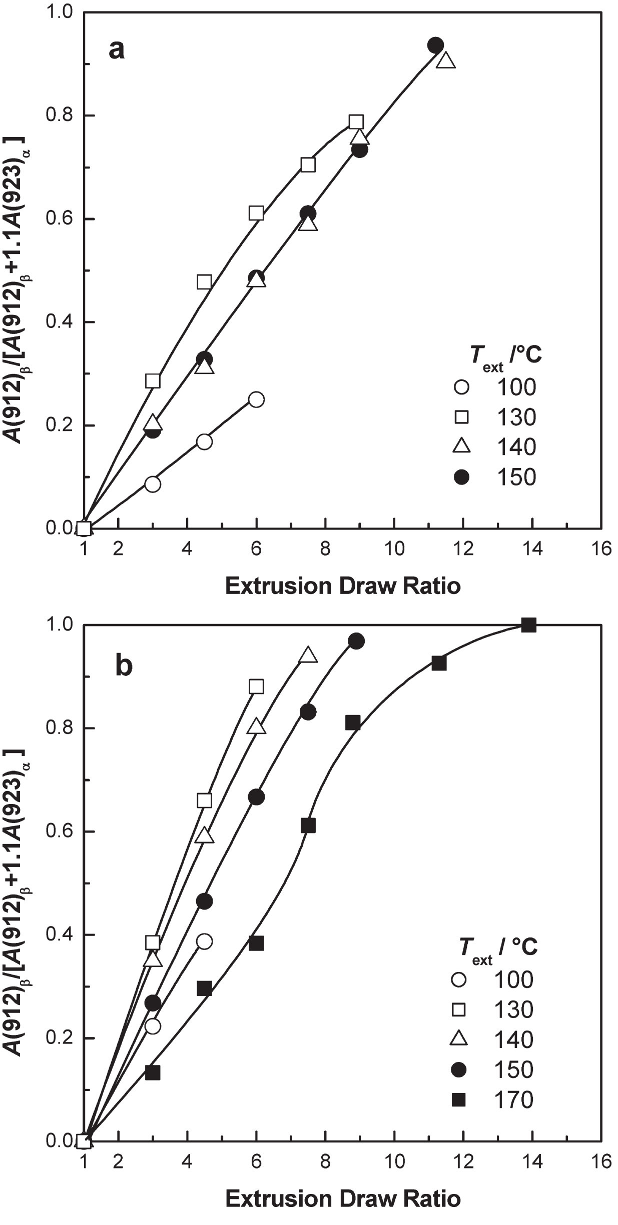

Figure 6.

Relative amounts of β-form crystals as a function of the EDR evaluated from the IR spectra of extrusion-drawn products prepared at different T_{ext}'s in the range of 100–170 °C: (a) L-M_v-2, and (b) H-M_v.

sample M_vs. It was noted that the strength at a given EDR was significantly higher for a higher molecular weight. The maximum achieved tensile strengths for these samples were significantly higher for a higher M_v; 120 MPa for L-M_v-1 having the lowest M_v and 500 MPa for the H-M_v having the highest M_v.

The maximum tensile modulus and strength that could be achieved in this work were 8 and 0.5 GPa, respectively. These tensile properties are comparable to

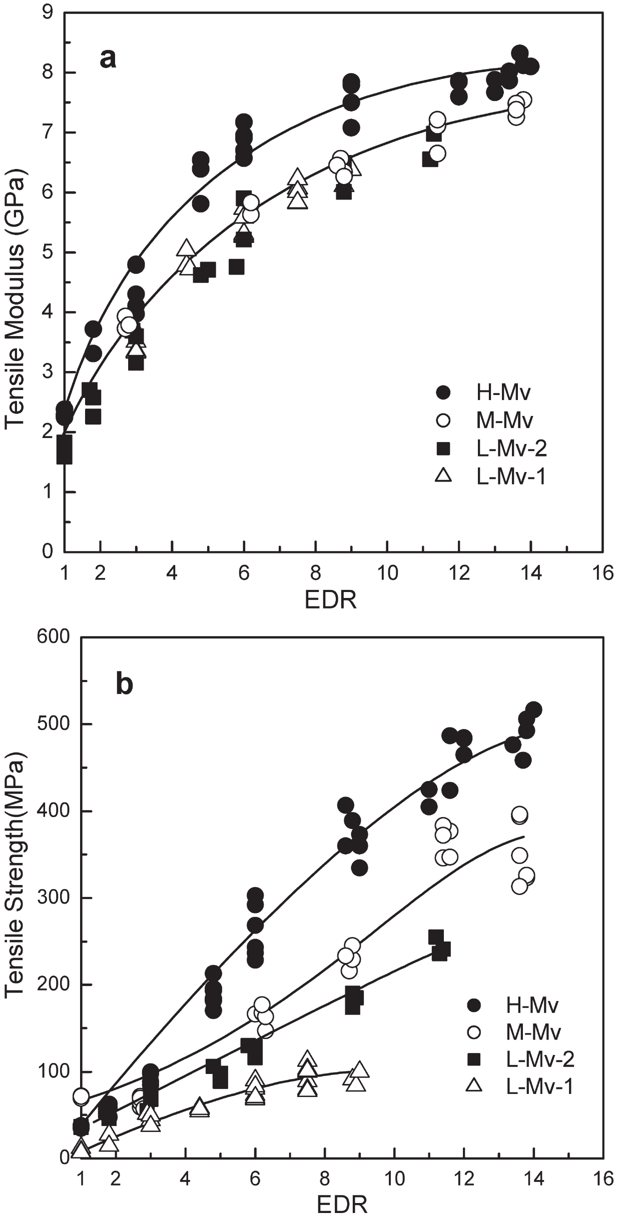

Figure 7.
Tensile modulus (a) and tensile strength (b) vs. EDR for solid-state coextrusion of various M_v's. The symbols are the same as in Figure 1.

the maximum moduli of 6–9.1 GPa and strength of 0.28–0.5 GPa, previously reported for drawing of melt-crystallized films of PLLA in the solid state below the T_m (170–180 °C). However, these values are significantly lower than the tensile moduli of 7–16 GPa and strength of 1–2.1 GPa achieved by the solution-spinning of a high molecular weight PLLA ($M_w = 9.1 \times 10^5$) followed by hot-drawing at 196.5–204 °C, significantly above the static T_m. Postema and Pennings[27] studied the effect of draw temperature (T_d) on the deformation mechanism of the solution-spun/hot-drawing.

They concluded that the deformation proceeded in the semicrystalline state up to $T_d = 180\,^\circ C$, and above this T_d the deformation proceeded in the liquid state of the polymer. Therefore, only under the controlled drawing rates and T_d's around $200\,^\circ C$, homogeneous draw could be achieved and high modulus and strength fibers could be obtained by applying low deformation rates so that the deformation took place in the liquid state of the polymer in which individual chains could be aligned, leading to a semicrystalline state by strain hardening after displacement of topological defects.

Nishino et al.[28] determined the crystal modulus of an α-form crystal of PLLA from the X-ray diffraction measurements of the actual strains of the crystals in the chain direction as a function of the applied stress. They reported 12 GPa for the crystal modulus of α-form in the chain direction. This crystal modulus is significantly lower than the fiber modulus of 16 GPa reported by Pennings et al.[27] Our preliminary examination of the crystal moduli of the α- and β-form crystals in the chain direction by using the X-ray diffraction method showed that the modulus of the α-form crystals determined on an as-drawn fiber was ~ 9 GPa and it increased to 13 GPa upon annealing the fiber neat the T_m. Although the crystal modulus of β-form was not significantly affected by the annealing and was ~ 12 GPa, the present observations suggest that the moduli of PLLA crystals are likely significantly affected by the processing conditons reflecting the crystal perfection. More details of the effects of crystal perfection on the crystal moduli of α- and β-form will be reported in the near future.

Conclusion

Melt-crystallized films prepared from the PLLA's with M_v's ranging from 3.8 to 46×10^4, were solid-state coextruded at T_{ext},s of 80–170 °C. To determine the effect of M_v on the crystal/crystal transformation form the α- to the β-form, the coextrusion-drawn products were characterized by IR spectroscopy and WAXD. The effect of M_v on the mechanical properties of coextrusion-drawn products was also measured by tensile tests.

The changes with the EDR in the relative intensities of the IR bands at 912 and 923 cm^{-1} showed that the crystal transformation from α- to β-form crystals proceeded with increasing the EDR and more rapidly for the higher M_v's. It was found that the crystal transformation proceeded most efficienciently at a T_{ext} around 130 °C, independently of the M_v's. As a result of the complex effects of the draw temperature, ductility and M_v's on the crystal transformation, however, highly oriented films consisting of β-form crystals alone were obtained by the coextrusion of H-M_v and M-M_v samples to higher EDR's > 11 in the T_{ext} range from 150 to 170 °C, near the $T_{m.}$

The maximum achieved draw ratio increased with increasing M_v. The tensile moduli at a agiven EDR were complarable, independently of the sample M_v's. However, the maximum achieved tensile modulus of 8.0 GPa was slightly higher for the highest M_v sample than those of 6.5–7.0 GPa for the lower M_v samples. The effect of sample M_v on the maximum achieved tensile strengths was significantly more prominent that that observed in the modulus, and 120 MPa for the lowest M_v of 3.8×10^4 and 500 MPa for the highest M_v sample of H-M_v. The highest modulus of 8.0 GPa and strength of 500 MPa were achieved at the highest EDR for the highest M_v sample of H-M_v.

Acknowledgement: This work was supported by an Industrial Technology Research Grant Program in '05 (05A52002c) from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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